ON THE RELATIVE STABILITY OF CUMULENONE AND ALDEHYDE ISOMERS: WHEN WE HEAT345(Q) THINGS UP

KELVIN LEE, *Radio and Geoastronomy Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; JOHN F. STANTON, *Department of Chemistry, The University of Texas, Austin, TX, USA*.

Isomers of $H_2C_{2n+1}O$ are examples of complex organic molecules that are either known or proposed to exist in the interstellar medium. For the smallest of these chains (H_2C_3O) only two of three isomers are observed in space: propynal ($HC(O)CCH$) and cyclopropenone ($c-C_3H_2O$), while evidence for the remaining isomer propadienone (H_2C_3O) is currently lacking. Potentially, this behaviour may be rationalised by a thermodynamic argument: several studies have provided quantum chemical calculations in an effort to determine the relative thermodynamic stability between these three isomers. An early study by Radom, at the SCF/6-31G** level ranked $HC(O)CCH$ as the thermodynamic minimum, followed by H_2C_3O, and $c-C_3H_2O$. The most recent determination by Karton and Talbi, using W2-F12 theory, places H_2C_3O as the lowest energy isomer; 2.5 kJ mol^{-1} lower than the $HC(O)CCH$ form. In an attempt to resolve this long-standing ambiguity, we were motivated to provide high level calculations based on the HEAT protocol. In this talk, we will discuss the relative stability of H_2C_3O and H_2C_5O isomers, along with their sulfur analogues, as revealed by HEAT345(Q) theory.